Effects of CNT addition on mechanical properties, electric conductivity and oxidation resistance of Al_2O_3-TiC composite

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Abstract. Effects of carbon nanotubes (CNT) addition on mechanical properties, electric conductivity and oxidation resistance of CNT/Al_2O_3-TiC composite were investigated. It was found that flexural strength, Young's modulus and fracture toughness of the composites were improved by addition of more than 2 vol%-CNT. In the composites with more than 3 vol%-CNT, the oxidation resistance of the composite was degraded. In comparison with Al_2O_3-26vol%TiC sample as TiC particle-percolated sample, the Al_2O_3-12vol%TiC-3vol%CNT sample, which is not TiC particle-percolated sample, shows almost the same mechanical properties and electric conductivity, and also shows thinner oxidized region after oxidation at 1200°C due to less TiC in the composite.

Introduction

Al_2O_3-TiC composites are widely used as cutting tools and substrate of magnetic head materials due to their attractive mechanical properties and good electric conductivity. Electric conductivity of the Al_2O_3-TiC composites increased rapidly as a TiC volume fraction increased from 0.20 to 0.23 [1]. The Al_2O_3-TiC composites exhibit electric conductivity of 10^{-1} $S \cdot m^{-1}$ and can be cut using wire discharge machining. However, due to the continuous TiC phase, oxidation of TiC proceeds continuously toward the inside of the composite.

Carbon nanotubes (CNTs) possess high mechanical properties, good electric conductivity and high aspect ratio. It is known that CNT/Al_2O_3 composites with a small amount of CNTs exhibit high mechanical properties [2] and good electric conductivity [3]. In this study, to fabricate CNT/ Al_2O_3-TiC composites with high mechanical properties, electric conductivity and excellent oxidation resistance, influence of CNT content on these properties of the composites was investigated.

Experimental

Al_2O_3, TiC and CNT were used as a starting powder. Commercially-available Al_2O_3 powder (0.15 μm, > 99.99%, Taimicron TM-DAR, Taimei Chemicals), TiC powder (1-2 μm, > 99 %, TiC-M, Japan New Metals) and various amounts of CNT powder were ball-milled for 20 h in ethanol. CNT was produced by using CCVD (catalytic chemical vapor deposition) method in the condition of 700°C for 1h in atmospheric H_2 carrier gas and C_2H_2 carbon source gas in the tubular electric furnace. Composition of the starting powder is listed in Table 1. The milled powders were then dried under vacuum and hot-pressed in a graphite die with a 25 x 25 x 3 mm^3 at 1700°C at 25 MPa under Ar for 1 h. Microhardness, flexural strength and Young's modulus were measured. For a part of specimens, fracture toughness was evaluated by indentation-fracture (IF) method. Electric resistance was measured by using a 4-probe electric resistance tester. Oxidation test was carried out in a thermogravimetric analyser, in N_2-20 vol.%O_2 with 50 $ml \cdot min^{-1}$

Table 1 Composition of CNT/ Al_2O_3-TiC composites

Sample name	composition [vol%]		
	Al_2O_3	TiC	CNT
AT12C0	87.6	12.4	0
AT12C1	86.7	12.3	1.0
AT12C2	85.8	12.2	2.0
AT12C3	84.9	12.0	3.0
AT12C5	83.2	11.8	5.0
AT26C0	84.0	26.0	0

from room temperature to 1200°C at a heating rate of 10°C·min^{-1}. Morphology observation and elemental analysis of the samples were performed using scanning electron microscope (SEM) and energy dispersive spectrometer (EDS).

Results and discussion

Porosity and mechanical properties. The porosity and the mechanical properties of all samples are presented in Fig. 1. The AT26C0 sample is described using solid circle with dotted horizontal line in the figures. The porosity of the samples increased with the increase of CNT content. The AT12C0 sample, which contains no CNT, shows small value in porosity compared with the AT26C0 sample (Fig.1 (a)). The CNT contents lessened the sintered densities of the nanocomposite [2], corresponding to the pores formed concerned with restricting sintering. The larger pores and agglomeration of CNTs can be observed in the sample containing relatively larger amount of CNT (Fig. 2 (a)). Vickers hardness of the samples decreased with the increasing CNT content (Fig.1 (b)). Higher TiC content in the Al_2O_3 matrix composites also deteriorated sinterability caused by covalent bond of TiC. The porous structure and CNT aggregates reduced not only the relative density but also hardness. The AT26C0 sample shows slightly higher value in hardness than that of the AT12C0, because TiC is relatively harder than Al_2O_3. However, significant 86% increases in flexural strength were obtained for the AT12C3 sample, in comparson with the AT12C0 sample (Fig.1 (c)). In contrast, relatively high drop (30%) in flexural strength were observed in the AT12C5 sample than that of the AT12C3 sample. The Young's modulus of the AT12C3 also shows the highest value of 127 GPa in Fig.1 (d). Whai, et al. revealed that addition of TiC in the Al_2O_3 matrix resulted in the increase in flexural strength and Young's modulus due to the improved fracture toughness [4]. The fracture toughness of the AT26C0 (7.3 MPa·m$^{1/2}$) is larger than that of AT12C0 (5.7 MPa·m$^{1/2}$). It is clearly observed that addition of CNTs in the Al_2O_3-TiC composite also improved the fracture toughness. The AT12C2 samples exhibited the highest value of 6.8 MPa·m$^{1/2}$. In general, conventional toughening mechanism for fiber-reinforced composites includes fiber pullout and crack bridging. From SEM observation, a few CNTs pullout in the samples observed in a crack formed after Vickers indentation test (Fig. 2 (b)).

Electric percolation by conductive materials. Fig. 3 shows the electric conductivity of sintered samples with volume fraction of CNT. The electric conductivity of the composites increases with the increase of CNT content, and exhibits a typical insulator-conductor transition between volume

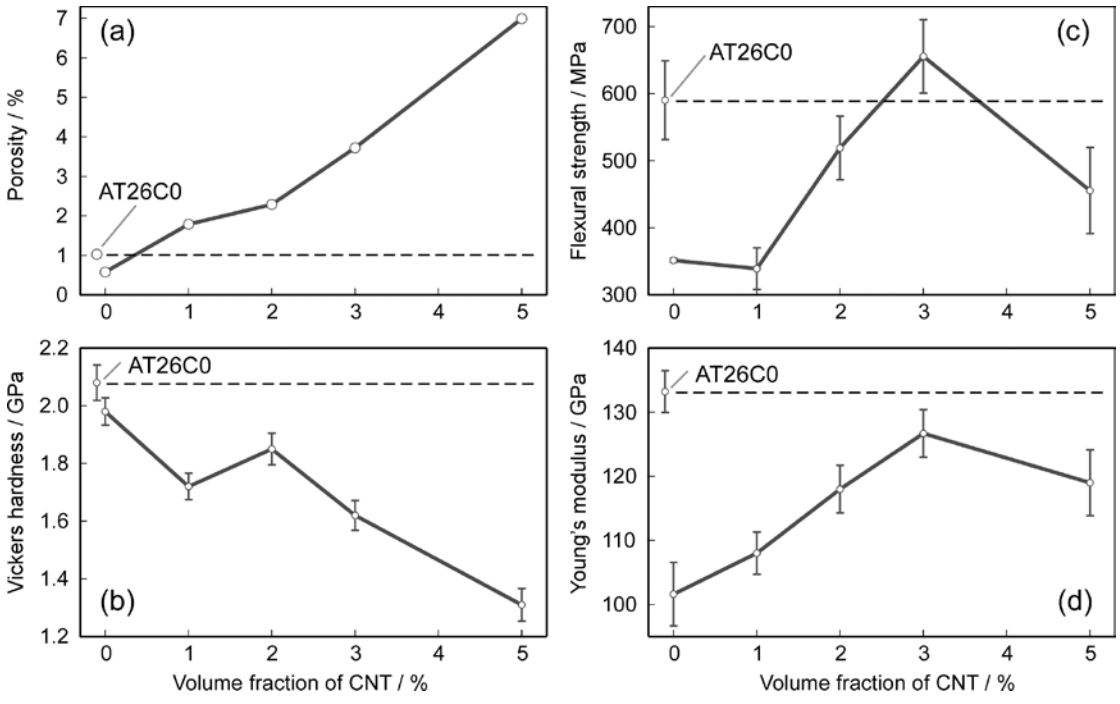

Fig. 1 Porosity and mechanical properties of sintered samples.

fraction of 1 and 3 vol.% of CNT. Because TiC and CNTs are metallic conductors, and Al_2O_3 is insulator, the electric percolation is achieved by forming CNT and TiC network in the Al_2O_3 matrix. The AT26C0 sample shows higher electric conductivity (4.6 $S \cdot m^{-1}$) than that of the AT12C0 sample ($2.6 \cdot 10^{-6}$ $S \cdot m^{-1}$). It was found that the percolation threshold concerning to the electric conductivity of the Al_2O_3-TiC composite was in the range of 0.20 to 0.23 in volume fraction of TiC [1]. Ahmad, et al. demonstrated that addition of MWNTs in Al_2O_3 matrix results in the dramatic increase of around eight orders of magnitude in the conductivity due to the percolation threshold in the well-dispersed MWNTs / alumina composites containing 0.45 mass% of MWNTs [3]. In this study, the AT12C2 sample containing 2 vol.%-CNT, which is about 1 mass%-CNT, is in a transition state of the electric conductivity. Considering the AT12C2 sample contains 12 vol.%-TiC, the electrical percolation formed CNT and TiC network in the Al_2O_3 matrix was estimated to occur at less than 1 vol.%-CNT content. It was thought that due to the agglomeration of CNTs and existence of pores in the sample respectively, more CNTs are needed to form the electrical percolation network.

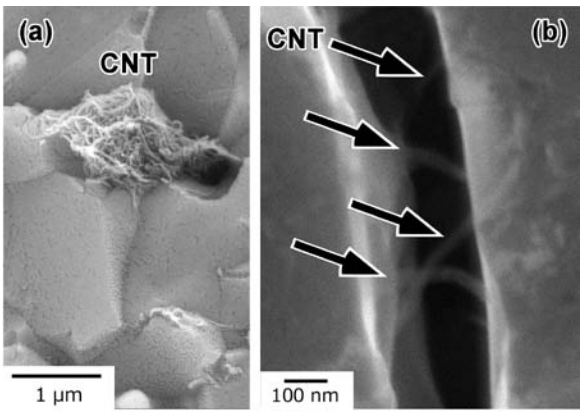

Fig. 2 Fractured surface (a) and crack (b) of the AT12C3 sample.

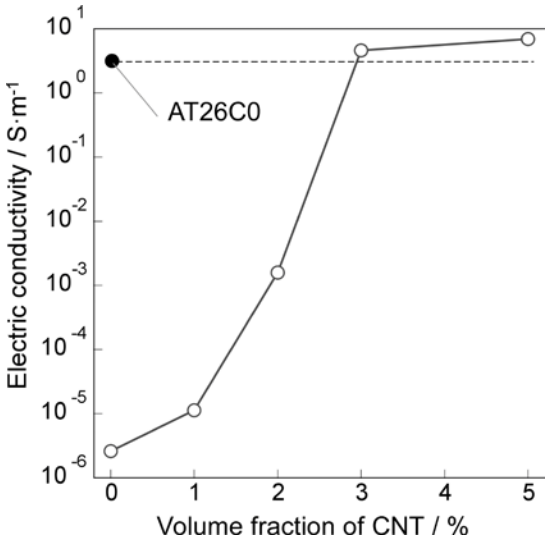

Fig. 3 Electric conductivity of sintered samples.

Oxidation resistance. Morphological change of the sample after oxidation is shown in Fig. 4. A few micrometers white TiC particle is embedded in the grayish Al_2O_3 matrix on the polished sample before oxidation. On the oxidized samples, it can be seen

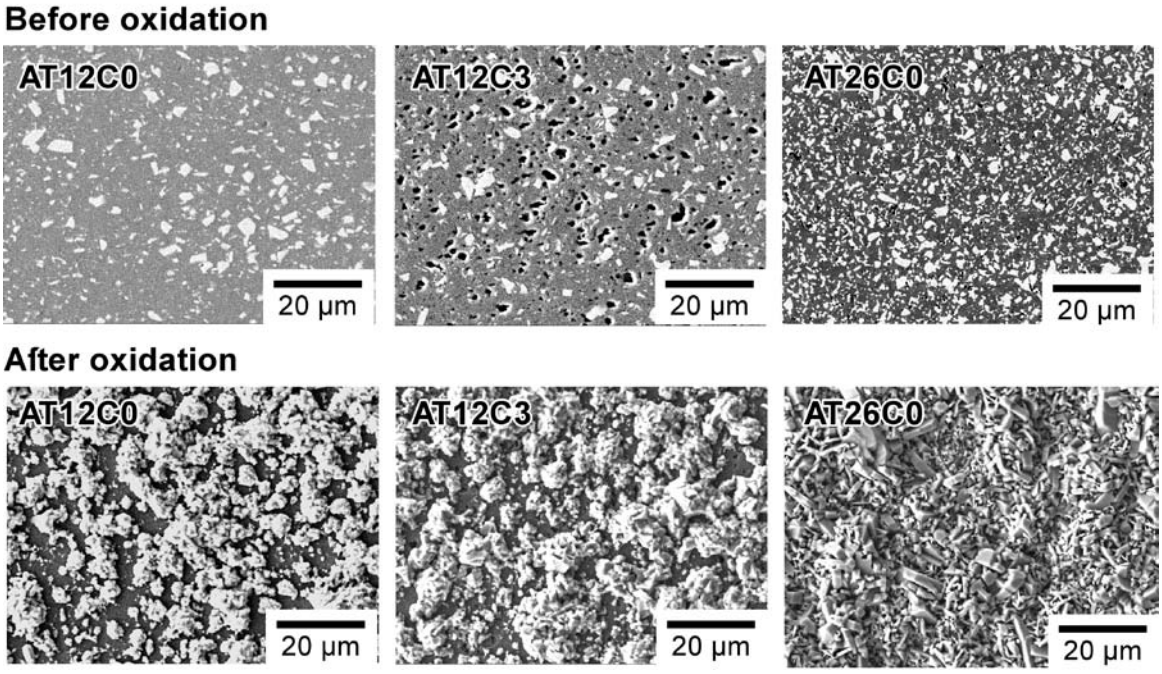

Fig. 4 Morphology of the sample before and after non-isothermal oxidation at 1200°C.

that several micrometers diameter grains, which agglomerate on the AT12C0 and AT12C3 sample, and are covered with the AT26C0 sample, appeared on the surfaces of these composites oxidized at 1200°C. Because oxidized grains were TiO_2 (rutile) detected by XRD, it can be attributed to the oxidation of TiC as a non-oxidized ceramics. During oxidation, TiC reacted with oxygen gas to produce not only TiO_2 but also carbon, which formed in circumstances of relative low partial pressure of oxygen of 10^{-30} atm considering from the Ellingham diagrams [5]. In the initial stage of oxidation, formed TiO_2 was on the TiC particle of the sample surface, and then, the oxidation proceeded toward the inside of the sample. The TiO gas might be formed during reaction due to the relative low partial pressure in the inside of the sample. TiC oxidation forming TiO gas results in the formation of pores in the sample nearby surface. In fact, cross sectional observation of oxidized sample showed that there is porous structure as an oxidized region in depth with 20 or 30 μm (Fig. 5). Value of depth of oxidized region was plotted in Fig. 6. The AT12C0, AT12C1 and AT12C2 show almost the sample value in the ranging from 8 to 10 μm. It was found that despite having a lot of pores in the AT12C3 sample, it has a good oxidation resistance compare with the AT26C0 sample with small amount of pores. As the AT26C0 sample has TiC particle-percolated structure, oxidation is easy to proceed. In contrast, the AT12C3 sample shows isolated embedded TiC particle in Al_2O_3 matrix, TiC particles connect via small amount of CNT with small diameter, therefore, there is less progress on oxidation in the AT12C3 sample.

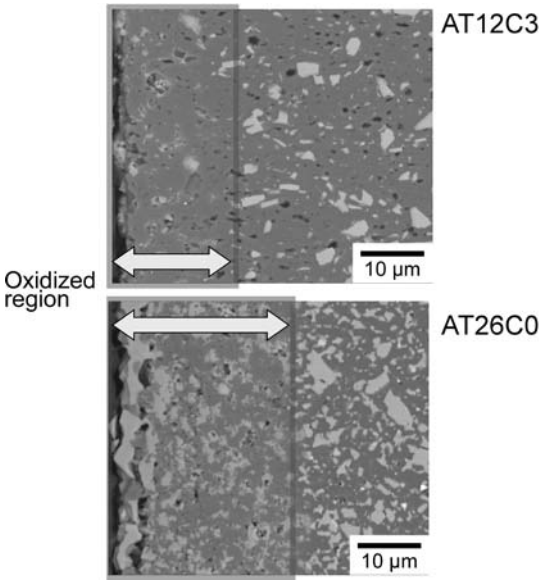

Fig. 5 Cross section of AT12C3 sample and AT26C0 sample after oxidation at 1200°C.

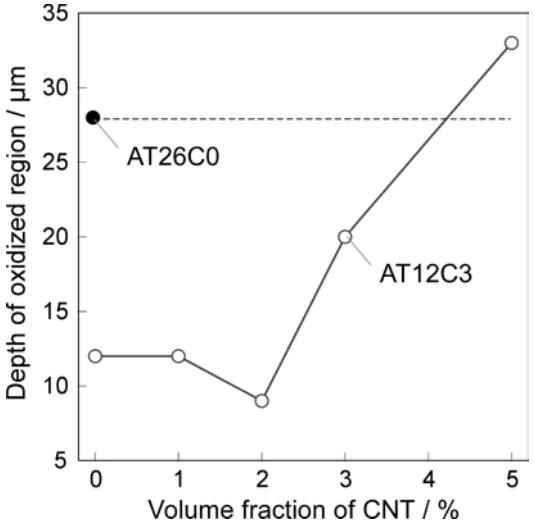

Fig. 6 Depth of oxidized region on the sample after oxidation.

Summary

The CNT/Al_2O_3-TiC composite with 3 vol.% CNTs exhibited high mechanical properties and good electric conductivity, and the composite exhibited less progress on oxidation compared with the Al_2O_3-TiC composite with electric conductivity via TiC.

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